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COMPOSITIONS BASED ON AN ETHYLENE-VINYL ALCOHOL
COPOLYMER AND POLYPROPYLENE

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~~[Field of the invention]~~

The present invention relates to compositions based on an ethylene-vinyl alcohol copolymer (EVOH) and polypropylene. EVOH copolymers are a barrier to many gases, and in particular to oxygen. Many articles of food packaging comprise a layer consisting of an EVOH film. Compositions based on EVOH and polyolefin and rich in EVOH also have good barrier properties. The compositions of the invention are useful for making barrier films in articles of food packaging.

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~~[The technical problem]~~

In general, EVOH copolymers have various excellent properties such as an oxygen impermeability property, mechanical strength, etc., and find application, as they are, in many uses such as films, sheets, materials for containers, textile fibers, etc. However, this copolymer gives rise to a variation in the thickness of the product in the moulding process for manufacturing a film or a sheet, with a consequent lowering of the commercializability of the product, and, because of the shortcoming in stretchability and flexibility, gives

rise to non-uniform drawing during deep drawing and other processes involving a stretching force, or pin holes during the use of the product, thus imposing serious limitations on its application as a raw material for packaging. Polyolefins may be added to EVOH, the blends obtained being more flexible and being more easily converted. However, it is not known how to add more than 20% whilst maintaining the barrier properties.

10 The oxygen barrier of EVOH copolymers is greatly reduced when the relative humidity (RH) increases, whereas blends of EVOH and polyolefin are less sensitive to relative humidity - a further reason for adding polyolefins to EVOH.

15 Another reason for adding polyolefins to EVOH is that polyolefins are generally much less expensive than EVOH.

One objective of the present invention is to prepare EVOH-based compositions containing as much polypropylene as possible, while at the same time maintaining good barrier properties.

25 Patent EP 418 129 discloses EVOH-based blends comprising 9.5 to 14.25% polypropylene and 5% compatibilizer. These blends are easily converted, the films obtained being used in packaging articles.

*T/S
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~~[Prior art]~~
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Patent EP 441 662 discloses the same blends but shows that the films obtained from these blends withstand hot water and steam better than pure EVOH films, that is to say the packaging articles comprising these films are resistant to sterilization. This advantage is important in the case of articles of food packaging. In both these patents, the ratio of the MFI of the EVOH to the MFI of the polypropylene is equal to 3, the MFIs being measured at 230°C under a load of 2.16 kg. The Applicant has tried to increase the proportion of polypropylene in the blend, but has not been able to convert it into film.

Patent EP 440 559 discloses blends of EVOH, polyolefin and compatibilizer. Comparative Example 4 shows a blend (by weight) of 60% EVOH, 35% polypropylene and 5% compatibilizer, that is to say the ratio of the amount of polypropylene to that of compatibilizer is equal to 7. The film obtained is not an oxygen barrier.

Patent EP 444 977 discloses blends of EVOH, polyolefin and compatibilizer. Comparative Example 4 shows a blend (by weight) of 55% EVOH, 20% polypropylene and 25% compatibilizer, that is to say the ratio of the amount of polypropylene to that of compatibilizer is equal to 0.8. The film obtained is not an oxygen barrier. In addition, in this blend the ratio of the MFI of the EVOH to the MFI of the polypropylene is equal to 0.29.

The Applicant has now discovered that, by choosing the ratio of the MFI of the EVOH to that of the polypropylene above 5 and by choosing the proportion of the compatibilizer and of the polypropylene so that the ratio of the amount of polypropylene to that of compatibilizer is between 1 and 5, blends of EVOH, polypropylene and compatibilizer possibly containing up to 45% polypropylene were obtained. In addition, these blends are easily convertible and are good oxygen barriers. Further advantages will appear below.

Ins
a ~~[Brief description of the invention]~~
as

The present invention relates to a composition comprising (by weight):

- 55 to 99.5 parts of an EVOH copolymer,
- 0.5 to 45 parts of polypropylene (A) and of compatibilizer (B), the proportions of (A) and (B) being such that (A)/(B) is between 1 and 5,
- the ratio of the MFI of the EVOH to the MFI of the polypropylene being greater than 5, "MFI" denoting the melt flow index.

a ~~[Detailed description of the invention]~~

The EVOH copolymer is also called a saponified ethylene-vinyl acetate copolymer. The saponified ethylene-vinyl acetate copolymer to be employed

according to the present invention is a copolymer having an ethylene content of 20 to 60 mol%, preferably 25 to 55 mol%, the degree of saponification of its vinyl acetate component not being less than 95 mol%.

5 With an ethylene content of less than 20 mol%, the oxygen impermeability property under high humidity conditions is not as high as would be desired, whereas an ethylene content exceeding 60 mol% leads to reductions in the oxygen impermeability property, in
10 the printability and in other physical properties. When the degree of saponification or of hydrolysis is less than 95 mol%, the oxygen impermeability property and the wet strength are sacrificed. Among these saponified copolymers, those which have melt flow indices in the
15 range of 0.5 to 100 g/10 minutes are particularly useful. Advantageously, the MFI is chosen between 10 and 30 (g/10 mm at 230°C/2.16 kg), while still satisfying the ratio with the MFI of the polypropylene.

It will be understood that this saponified
20 copolymer may contain small proportions of other comonomer ingredients, including α -olefins such as propylene, isobutene, α -octene, α -dodecene, α -octadecene, etc., unsaturated carboxylic acids or their salts, partial alkyl esters, complete alkyl esters,
25 nitriles, amides and anhydrides of the said acids, and unsaturated sulphonic acids or their salts.

The oxygen permeability of the EVOH copolymer films which is measured according to ASTM D 3985 is

expressed in cm^3 of oxygen per m^2 per 24 hours for a pressure difference of 1 bar and a thickness of 25 μm . To simplify matters, it will be denoted in the rest of the text as O_2GTR .

5 O_2GTR varies proportionally with the inverse of the film thickness.

 An EVOH comprising 38 mol% of ethylene units has an O_2GTR of 0.72 for 0% RH and 3.1 for 75% RH.

 An EVOH comprising 29 mol% of ethylene units has
10 an O_2GTR of 0.1 for 0% RH and 1.41 for 75% RH. These grades are produced on an industrial scale and are commercially available.

 One or other of these grades is used in different thicknesses depending on the barrier required (nature
15 of the product to be preserved, preservation time, etc.).

 With regard to (A), this is a polypropylene, homopolymer or copolymer, the copolymer possibly being of the block or random type. With regard to copolymers,
20 the copolymer may be chosen from alpha-olefins having up to 30 carbon atoms. By way of examples of alpha-olefins, mention may be made of 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene,
25 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1-octacocene and 1-triacontene. These alpha-olefins may be used by themselves or as a mixture of two or more of them.

The comonomer may also be a diene. (A) may be blended with EPR (the abbreviation for Ethylene-Polypropylene-Rubber, an ethylene-propylene elastomer) or with EPDM (the abbreviation for Ethylene-Polypropylene-Diene Monomer, an ethylene-polypropylene-diene elastomer).

Advantageously, the polymer (A), which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of propylene.

Advantageously, the MFI of (A) is between 0.5 and 3 (in g/10 mm at 230°C/2.16 kg) and preferably 1 to 2.5, while still, of course, satisfying the condition of the MFI ratio with EVOH.

The MFIs used in the ratio of the MFI of the EVOH to the MFI of the polypropylene are measured under the same temperature conditions and under the same load. Advantageously, the measurement is carried out at 230°C under a load of 2.16 kg. According to an advantageous embodiment, this ratio is between 5 and 25 and preferably between 8 and 15. Values above 25 or even between 30 and 40 are possible, but they are of little interest because the corresponding EVOH-based compositions are not always reproducible.

As regards the compatibilizer (B), this is any polymer allowing the polypropylene to be dispersed in the EVOH. By way of example, mention may be made of functionalized polyolefins such as ethylene homopolymers or maleic-anhydride-grafted copolymers,

propylene homopolymers or maleic-anhydride-grafted copolymers and maleic-anhydride-grafted EPR or EPDM elastomers. Advantageously (B) is either a polyethylene carrying polyamide grafts or a polypropylene carrying polyamide grafts.

With regard to polyethylene carrying polyamide grafts, this results from the reaction of (i) a copolymer (B1) of ethylene and an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2). The starting point is the preparation of (B1), which is either a copolymer of ethylene and an unsaturated monomer X, or a polyethylene onto which an unsaturated monomer X is grafted. X is any unsaturated monomer that can be copolymerized with ethylene or grafted onto polyethylene and having a functional group that can react with a polyamide. This functional group may be a carboxylic acid, a dicarboxylic acid anhydride, an epoxy, etc.

By way of examples of monomer X, mention may be made of (meth)acrylic acid, maleic anhydride, unsaturated epoxides such as glycidyl (meth)acrylate, etc. Advantageously, maleic anhydride is used.

With regard to polyethylenes onto which X is grafted, polyethylene is understood to mean homopolymers or copolymers.

By way of comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms - they were mentioned above and also include polypropylene;

- the esters of unsaturated carboxylic acids, such as, for example, alkyl (meth)acrylates, the alkyls possibly having up to 24 carbon atoms; examples of alkyl acrylates or methacrylates are, especially, methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;

10 - vinyl esters of saturated carboxylic acids, such as, for example, vinyl acetate or vinyl propionate;

- dienes such as, for example, 1,4-hexadiene.

- the polyethylene may include several comonomers.

Advantageously, the polyethylene, which may be a
15 blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of ethylene and its density may be between 0.86 and 0.98 g/cm³. The MFI (viscosity index at 190°C/2.16 kg) is advantageously between 1 and 1000 g/10 min.

20 By way of example of polyethylenes, mention may be made of:

- low-density polyethylene (LDPE);

- high-density polyethylene (HDPE);

- linear low-density polyethylene (LLDPE);

25 - very low-density polyethylene (VLDPE);

- polyethylene obtained by metallocene catalysis,

that is to say polymers obtained by the

copolymerization of ethylene and an alpha-olefin such

as propylene, butene, hexene or octene in the presence of a single-site catalyst generally consisting of a zirconium or titanium atom and of two alkyl cyclic molecules linked to the metal. More specifically, 5 metalocene catalysts are usually composed of two cyclopentadiene rings linked to the metal. These catalysts are frequently used with aluminoxanes as cocatalysts or activators, preferably methyl aluminoxane (MAO). Hafnium may also be used as the 10 metal to which the cyclopentadiene is fixed. Other metallocenes may include transition metals of Groups IVA, VA and VIA. Metals from the series of lanthanides may also be used;

- EPR (ethylene - propylene - rubber) elastomers;
 - 15 - EPDM (ethylene - propylene - diene) elastomers;
 - blends of polyethylene with an EPR or an EPDM;
 - ethylene-alkyl (meth)acrylate copolymers
- possibly containing up to 60%, and preferably 2 to 40%, by weight of (meth)acrylate.

20 The grafting is an operation known per se.

With regard to the copolymers of ethylene and monomer X, that is to say those in which X is not grafted, these are copolymers of ethylene and X and optionally another monomer, which can be chosen from 25 the comonomers mentioned above in the case of the ethylene copolymers to be grafted by X. Advantageously, ethylene-maleic anhydride and ethylene-alkyl (meth)acrylate-maleic anhydride copolymers are used.

These copolymers comprise from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate. Their MFI is between 1 and 50 (190°C - 2.16 kg). The alkyl (meth)acrylates have already been described above.

Polyamide (B2) should be understood to mean the products of the condensation:

- of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids of one or more lactams, such as caprolactam, oenantholactam and lauryllactam;

- of one or more salts or mixtures of diamines, such as hexamethylenediamine, dodecamethylenediamine, metaxylylenediamine, bis(p-aminocyclohexyl)methane and trimethylhexamethylenediamine with diacids, such as isophthalic, terephthalic, adipic, azeleic, suberic, sebacic and dodecanedicarboxylic acids;

- or of mixtures of several monomers, thereby resulting in copolyamides.

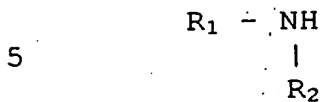
Blends of polyamides may be used. Advantageously, PA-6, PA-11, PA-12, the copolyamide containing nylon-6 units and nylon-12 units (PA-6/12) and the copolyamide based on caprolactam, hexamethylenediamine and adipic acid (PA-6/6.6) may be used.

(B2) is a polyamide or a polyamide oligomer.

Polyamide oligomers are described in EP 342 066.

The polyamides (B2) may have acid, amine or monoamine terminal groups. For the polyamide to have a

monoamine terminal group, all that is required is to use a chain stopper of formula:



in which:

10 R_1 is hydrogen or a linear or branched alkyl group containing up to 20 carbon atoms;

R_2 is a group having up to 20 linear or branched, alkyl or alkenyl carbon atoms, a saturated or unsaturated cycloaliphatic radical, an aromatic radical or a combination of the above. The stopper may, for
15 example, be laurylamine or oleylamine.

 Advantageously, (B2) is a PA-6, a PA-11 or a PA-12. According to another advantageous embodiment of the invention (B2) is a monoaminated oligomer of PA-6, preferably having a mass of between 1000 and 3500.

20 The proportion of (B2) in B1 + B2 by weight is advantageously between 0.1 and 60%.

 The reaction of (B1) with (B2) preferably takes place in the molten state. (B1) and (B2) may, for example, be mixed in an extruder at a temperature
25 generally of between 230 and 250°C. The average residence time of the melt in the extruder may be between 10 seconds and 3 minutes, and preferably between 1 and 2 minutes.

 With regard to (B), a polypropylene carrying
30 polyamide grafts, this results from the reaction of (i)

a propylene homopolymer or copolymer (B3) comprising an unsaturated monomer X, which is grafted or copolymerized, with (ii) a polyamide (B2).

The process starts with the preparation of (B3) which is either a copolymer of propylene and an unsaturated monomer X, or a polypropylene onto which an unsaturated monomer X is grafted. X is any unsaturated monomer that can be copolymerized with propylene or grafted onto polypropylene, and possessing a functional group that can react with a polyamide. This functional group was defined above. With regard to grafted polypropylenes, X may be grafted onto propylene homopolymers or copolymers, such as ethylene-propylene copolymers containing predominantly propylene (in terms of moles). Grafting is an operation known per se. With regard to (B3) in which X is grafted, X may be firstly grafted in the same extruder, in the first zones, and then the product (B2) may be introduced a few zones further downstream. (B2) was defined above.

The reaction between (B3) and (B2) takes place under the same conditions as the reaction between (B1) and (B2).

Advantageously, the ratio (by weight) of (A) to (B) is between 2 and 4.

The blends of the invention may be prepared by melt blending in extruders (single-screw or twin-screw), Buss kneaders, Brabender mixers and, in general, the usual devices for blending thermoplastics.

The compositions according to the invention may furthermore contain at least one additive chosen from:

- dyes;
- pigments;
- 5 - brighteners;
- antioxidants;
- UV stabilizers.

The invention also relates to the films consisting of the above compositions, to the multilayer structures comprising a film or a layer consisting of the above
10 compositions and to the packaging articles comprising these structures.

According to one embodiment, the invention provides a film comprising at least one layer of a
15 composition according to the invention and at least one adjacent polypropylene layer. The adhesion between these two layers is good. This film may especially be produced by coextrusion.

The polypropylene is a polypropylene homopolymer
20 or copolymer. As comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 4 to 30 carbon atoms;
- dienes.

The polypropylene may also be a copolymer having
25 polypropylene blocks.

As examples, mention may be made of:

- polypropylene homopolymer;

- polypropylene/EPDM or polypropylene EPR blends possibly also containing 1 to 20% polyethylene.

Advantageously, the polypropylene, which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of propylene.

The polypropylene has, for example, an MFI of between 20 and 40 g/10 min (230°C/2.16 kg).

[Examples]

10

The following materials were used:

15

EVOH E ethylene-vinyl alcohol copolymer containing 38 mol% of ethylene, having an MFI of 8 (210°C/2.16 kg), a melting point of 183°C, a crystallization temperature of 160°C and a T_g (glass transition temperature) of 61°C;

20

EVOH D ethylene-vinyl alcohol copolymer containing 29 mol% of ethylene, having an MFI of 15 (230°C/2.16 kg), a melting point of 188°C, a crystallization temperature of 163°C and a T_g (glass transition temperature) of 62°C;

25

EVOH DC ethylene-vinyl alcohol copolymer containing 32 mol% of ethylene, having an MFI of 6 (230°C/2.16 kg), a melting point of 188°C, a crystallization

temperature of 163°C and a T_g (glass transition temperature) of 62°C;

5' PP 3020 GN 3 polypropylene supplied by Appryl®, a random copolymer having a melting point of 148°C (10°C/minute) and an MFI of 1.8 (230°C/2.16 kg);

10 PP 3010 GN 5 polypropylene supplied by Appryl®, a block copolymer having a melting point of 163°C (10°C/minute) and an MFI of 1.4 (230°C/2.16 kg);

VESTOLEN P9000® polypropylene supplied by Hüls, having an MFI of 2 (230°C/2.16 kg);

15 MOPLEN random polypropylene containing 3% ethylene and having an MFI of 2 (230°C/2.16 kg);

20 COMP 1 compatibilizer, an ethylene-polypropylene copolymer containing 88 mol% of polypropylene grafted by 1% of maleic anhydride and then condensed with a monoaminated nylon-6 oligomer of 2500 mass;

25 COMP 2 compatibilizer, an ethylene-polypropylene copolymer containing 88 mol% of polypropylene grafted by 1% of maleic anhydride.

The blends were produced on a Buss 15D kneader.

The results are given in Table 1 below, in which the proportions are by weight.

TABLE 1

Examples (comparative examples marked #)	1 #	2 #	3 #	4 #	5	6	7	8	9
EVOH E		100							
EVOH DC			80	80					
EVOH D	100				80	80	60	60	60
PP 3020 GN3								30	
PP 3010 GN5							30		30
VESTOLEN P9000						15			
MOPLIN			15	15	15				
COMP 1			5		5	5	10	10	
COMP 2				5					10
EVOH MFI/(A) MFI at 230°C/2.16 kg			3	3	7.5	37.5	10.7	8.3	10.7
O ₂ GTR (0% RH, 23°C)	0.08	0.7	0.3	0.3	0.2	0.1	0.4	0.3	0.4
O ₂ GTR (75% RH, 23°C)	1.1	3	1.4	1.4	1	1.2	2	2	5.4
O ₂ GTR (75% RH)/O ₂ GTR (0% RH) ratio	14	4	5	5	5	12	5	6	13